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Nalco Docket No. 7774
Customer No. 49459In the United States Patent and Trademark Office

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|-------------|-------------------------|---|-----------|---------------------|
| Applicants: | Brian T. Holland et al. |) | Examiner: | Daniel S. Metzmaier |
| | |) | | |
| Serial No.: | 10/827,214 |) | Art Unit: | 1796 |
| | |) | | |
| Date Filed: | April 19, 2004 |) | | |

For: COLLOIDAL COMPOSITIONS AND METHODS OF PREPARING SAME

Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

**DECLARATION OF PRIOR INVENTION IN THE UNITED STATES OR IN A NAFTA OR
WTO MEMBER COUNTRY TO OVERCOME CITED PATENT OR PUBLICATION
UNDER 37 C.F.R. § 1.131**

Dear Sir:

This Declaration is to establish completion of the invention in this application in the United States prior to December 5, 2003, the effective date of Cundy et al., "Some observations on the preparation and properties of colloidal silicates. Part I: synthesis of colloidal silicalite-1 and titanossilicalite-1 (TS-1)," Microporous and Mesoporous Materials, 66 (2003): 143 to 156 ("Effective Date of Cundy").

To establish a date of completion of this invention prior to the Effective Date of Cundy, Applicants submit herewith copies of research notebook pages attached as Exhibit A hereto. This exhibit clearly and definitely establishes invention of the subject matter of the currently rejected claims prior to the Effective Date of Cundy.

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Applicants declare that the document submitted herewith as Exhibit A is dated prior to December 5, 2003. Accordingly, Applicants respectfully assert that this invention was completed prior to the Effective Date of Cundy.

Explanations of the experiments portrayed on pages 1 to 3 of Exhibit A is provided below:

Notebook Page 3 [Page 1 of Exhibit A]

Preparation of Ce₂O₃-SiO₂ co-sol

Ce(III) stock solution:



$$\frac{\text{Ce}_2\text{O}_3}{2 \text{ Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}} = \frac{328.24}{868.46} = 0.3779$$

For 5%Ce₂O₃ solution:

$$5/0.3779 = 13.23 \text{ g of cerium nitrate in 100g}$$

Synthesis: Acid sol or silicic acid was prepared by deionizing sodium silicate. The yield was 1.1 kg of acid sol with a specific gravity of 1.042. Silica concentration was calculated using the equation:

$$\% \text{SiO}_2 = \text{Specific gravity} * 163.2207 - 163.1891$$

$$\text{Total silica} = 1.1 * 6.88\% = 75.75 \text{ g}$$

0.75 g CeO₂ is 1%, thus 15g of Ce stock solution was needed.

The acid sol had a 3.05 pH and a 195μS conductance, with the addition of the acidic Ce solution these changed to 2.95 and 980 respectively. This blend was a true solution of ionic Ce(III) and monomeric silicic in an aqueous medium. The complete incorporation of both species in solution is the basis for the homogeneous formation of the corresponding colloidal oxides under the high pH reaction conditions.

- Heel – 200 ml of deionized water and 0.7 g of 45% KOH solution; pH 13.34. Heated to 75°C with steering.

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- Feed – The acid sol/Ce was fed to the heel at 3.66 ml/min once the temperature in the heel reaches 76°C. The pH is monitor; after 1:15 the pH has dropped from the original 11.3 to 7.9. At this time a solution of 0.1N KOH was co-fed to maintain the pH above 7.3. After 4:57 hours both solutions have been added, final pH is 7.3 at 75°C. Heating with stirring continued for 2 hours.
- Concentration – The 2 liter pinkish sol was concentrated to 300 ml by ultra filtration. The filtrate was colorless, indicating that all the Ce was in the colloidal particles

Notebook Pages 17 and 18 [Pages 2 and 3 of Exhibit A]

Preparation of $\text{TiO}_2\text{-SiO}_2$ co-sol

Synthesis: 1100 g of acid sol was prepared from sodium silicate. Specific gravity was 1.04, corresponding to 6.56% SiO_2 .

Total silica = $1.1\text{kg} * 6.56\% = 72.42\text{g}$

2% $\text{TiO}_2 = 1.44\text{ g TiO}_2$

TiO_2 solutions prepared from TiOSO_4 formed a precipitate with time; so it was not practical to store the solutions.

A solution of 3.3g of 87% $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ was dissolved in 150 ml of deionized water and was added to the acid sol. This homogeneous metal and silicic acid solution was used as feed for the colloidal particle synthesis.

- Heel – 200 ml of deionized water and 0.7 g of 45% KOH, 12.47 pH at room temperature. Heated with steering to 77°C.
- Feed – The silica-Ti solution is added to the heel at 3.66 ml/min. After 30 minutes a co-feed of 0.1N KOH started. At the end of the reaction, 4 1/2 hours, a total of 500 ml KOH were added. The sol was refluxed for one hour
- The dilute sol was milky white and was concentrated by ultra filtration. The excess ions were washed out by dial filtration. Three 1-liter filtrates are collected. Analyses confirmed that the TiO_2 was incorporated into the colloidal particle.

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| Ion | SiO ₂ | Na | K | SO ₄ | Ti |
|--------------------------|------------------|-----|-----|-----------------|-------|
| ppm | | | | | |
| 1 st filtrate | 350 | 6.4 | 440 | 920 | 7.9 |
| 2 nd filtrate | 200 | 4.6 | 300 | 630 | 3.2 |
| 3 rd filtrate | 87 | 2.4 | 150 | 340 | 0.9 |
| Sol | | | 880 | 190 | 1,200 |

The resultant sol was stable for over two years.

DECLARATION

As a person signing below, I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: 1/11/10

Signed: 

Yolanda Ortiz

Exhibit A

Page 1 of 3

TITLE $\text{Ce}_2\text{O}_3/\text{SiO}_2$

PROJECT NO.

BOOK NO.

3

Preparation of $\text{Ce}_2\text{O}_3\text{-SiO}_2$ Co-sol

$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ \rightarrow Ce_2O_3 Ce_2O_3 $328.24 = 375.9$
 424.23 328.24 $2 \text{ Ce}(\text{NO}_3)_3$ 867.46

5% Ce_2O_3 soln; $5/375.9 = 13.23 \text{ g}$ of substrate
 $\text{pH} = 7.12$

NO_3 186 3 mg NO_3 0.0069 mg/g
 $\text{Ce}(\text{NO}_3)_3$ 424.23 439.235 0.091 mg/g 1% soln
 $= 0.428 \times 13.23 \text{ g} = 5.66 \text{ g}$ NO_3 0.91 mg/g 100 g of 5% Ce_2O_3
 KOH 0.9 mg/g

7 g KOH $+ 200 \text{ ml}$ DIW $\text{pH} = 13.34$ $T = 19.5$

AS 1.12 11 kg $\text{pH} = 9.05$ $C = 195$ $T = 98.0$

SA 2.042 6.88 $\text{SiO}_2 \times 11 \text{ kg}$ $75.75 \text{ g} \times 1\% = 7.57 \text{ g}$ Ce_2O_3 11.15 g Ce_2O_3 soln

| T | W | ENW | pH | T |
|------|------|------|-----|---|
| 9:30 | 33.7 | 9.92 | 7.6 | 3.66 ml/min |
| 2:01 | 95 | 9.26 | 7.4 | turn |
| 1:02 | 223 | 8.23 | 7.3 | 125 ml DIW KOH in place |
| 1:15 | 200 | 7.9 | | add KOH starts |
| 1:29 | 322 | 8.21 | 7.3 | 50 ml on 5 mg |
| 1:53 | 411 | 7.79 | 7.5 | 75 |
| 2:09 | 467 | 7.85 | 9 | 90 |
| 2:27 | 535 | 7.99 | 9 | 125 |
| 3:10 | 689 | 7.35 | | 5 |
| 3:24 | 738 | 7.40 | | 40 |
| 3:45 | 816 | 7.44 | | 75 |
| 4:02 | 875 | 7.60 | | 93 |
| 4:18 | 906 | 7.30 | | 105 |
| 4:57 | 1075 | 7.30 | | 125 |

heated an ultra flow

$2/6$ $\text{pH} = 7.30$ $T = 19.5$ SiO_2 ppt on and desirable

$\text{pH} = 7.30$ $C = 940$ $\text{pH} = 7.50$ $T = 98.0$ $\text{pH} = 7.50$ $T = 98.0$

100 ml DIW KOH $\text{pH} = 7.50$ $T = 98.0$ $\text{pH} = 7.50$ $T = 98.0$

1 g Ce_2O_3 $\text{pH} = 7.50$ $T = 98.0$ $\text{pH} = 7.50$ $T = 98.0$

1 g Ce_2O_3 $\text{pH} = 7.50$ $T = 98.0$ $\text{pH} = 7.50$ $T = 98.0$

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Exhibit A
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TITLE $\text{SiO}_2/\text{TiO}_2$
Co - Sol

PROJECT NO.
BOOK NO.

17

Residue with TiO_2SO_4

AS = 1100g $C = 215$ miles $\text{pH} = 2.32$
 Sp. Gr. 1.04 6.56% SiO_2
 Non 6.56% = 72.48g SiO_2 $\times 2\% \text{TiO}_2 = 1.44\text{g}$ 1.10g
 $\Rightarrow 3.3\text{g}$ $\text{TiO}_2\text{SO}_4 \times \text{H}_2\text{O}$ from GFS 150g 3rd
 after 40 AS $\Rightarrow \text{pH} = 1.70$ $C = 950$ $T_1 = 863\text{mg}$

Next
 0.75 KOH $\text{pH} = 1.70$ 11.05
 500 ml SiO_2 12.47g H_2O 70°C

| t | val | pH | T | |
|------|------|-------|-----|-----------------------------|
| 0 | 0 | 12.05 | 77C | 3.66 ml/min |
| 10 | 37 | 9.55 | 72 | |
| 50 | 72 | 8.90 | 72 | |
| 32 | 112 | 7.96 | 73 | addition of 0.1N KOH starts |
| 41 | 151 | 7.20 | | 20 ml added |
| 1:06 | 241 | 6.34 | | 50 |
| 1:13 | 267 | 5.84 | 73 | 50 |
| 1:25 | 312 | 6.2 | | 100 Freshly distilled water |
| 1:50 | 402 | 6.8 | | 185 |
| 2:13 | 485 | 7.12 | 74 | 250 |
| 2:25 | 531 | 6.79 | | 250 ml more in the front |
| 2:40 | 589 | 6.42 | 74 | 15 |
| 3:03 | 676 | 6.80 | | 100 |
| 4:00 | 878 | 6.67 | 72 | 225 |
| 4:37 | 1021 | 6.17 | 74 | 250 |
| 5:45 | | 6.24 | | stop |
| 3:15 | | 7.10 | 77 | Replaced for 1-hr |

Very turbid, no ppt on gel
 $\text{pH} = 6.5$ $C = 1310$
 V.F. plate

3/28 Filter very slow

7 1st filtrate 350 ml $\text{pH} = 5.60$ $C = 1350$
 500 ml added to the cell
 9 2nd filtrate 950 ml $\text{pH} = 5.76$ $C = 950$
 4/15 3rd filtrate
 710 ml $\text{pH} = 6.15$ $C = 520$

Continued pg 18

SIGNATURE

DATE

READ AND UNDERSTOOD BY

DATE

cep

Cheryl Slobogoshi

Exhibit A
Page 3 of 3

18

TITLE

PROJECT NO.

BOOK NO.

Concentrate

Very thick, but fluid opaque

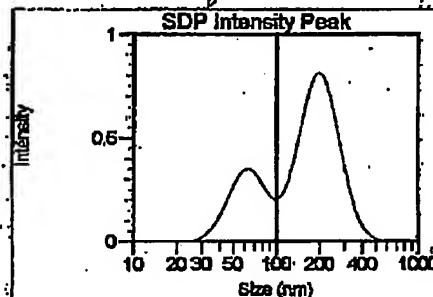
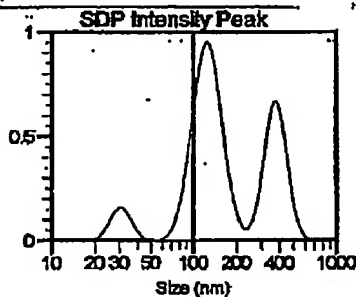
300 ml 304 g C-6.55

set in test tube @
60°C as 18A

A

pH = 6.53
Another test tube adjusted to pH = 10.3 w/NaOH
gave to oven 400°C as 18BAfter overnight @ 60°C samples look like gel
but re-disperse when shaken
18A: re-dispersed 18B: re-dispersed both w/shaking

DLS data

114.2 ± 49 nm
poly 0.701138.3 ± 56.8 nm
poly 0.701

| Amount | Size (nm) | SD (nm) |
|--------|-----------|---------|
| 60.8% | 121.3 | 22.8 |
| 31.9% | 363.3 | 49.9 |
| 7.3% | 29.4 | 3.9 |

| Amount | Size (nm) | SD (nm) |
|--------|-----------|---------|
| 70.7% | 186.4 | 50.8 |
| 29.3% | 61.8 | 15.4 |

A Concentrate

B dilute pH adjusted

Analyses Report

| | SiO ₂ | Na | K | SO ₄ |
|----------|------------------|-----|-----|-----------------|
| 1st fill | 350 | 6.4 | 490 | 92.57 |
| 2nd | 200 | 4.6 | 300 | 630 |
| 3rd | 87 | 2.4 | 150 | 340 |

| | T ₆ | T ₇₋₉ |
|----------|----------------|------------------|
| 1st fill | 13.2 | 0.91 |
| 2nd | 1200 | 1200 |
| 3rd | 950 | 950 |

Sol heat dist.

Sol heat conc.

RT samples both

Thick, re-disperse

w/shaking

Stable after 2 years

SIGNATURE

DATE

READ AND UNDERSTOOD BY

DATE

UPP

[Redacted]

Chen Shubaozhi

[Redacted]